CO$_2$ Capture

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Multi-Molar Absorption of CO$_2$ by the Activation of Carboxylate Groups in Amino Acid Ionic Liquids

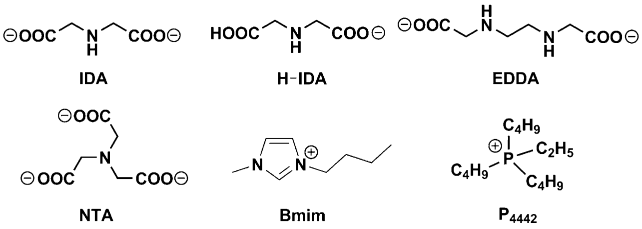
Feng-Feng Chen[+]*, Kuan Huang*[+]*, Yan Zhou, Zi-Qi Tian, Xiang Zhu, Duan-Jian Tao,* De-en Jiang, and Sheng Dai**

Abstract: *A new strategy for multi-molar absorption of CO$_2$ is reported based on activating a carboxylate group in amino acid ionic liquids. It was illustrated that introducing an electron-withdrawing site to amino acid anions could reduce the negative inductive effect of the amino group while simultaneously activating the carboxylate group to interact with CO$_2$ very efficiently. An extremely high absorption capacity of CO$_2$ (up to 1.69 mol mol^{-1}) in aminopolycarboxylate-based amino acid ionic liquids was thus achieved. The evidence of spectroscopic investigations and quantum-chemical calculations confirmed the interactions between two kinds of sites in the anion and CO$_2$ that resulted in superior CO$_2$ capacities.*

The emission of CO$_2$ from the combustion of fossil fuels has become an urgent issue because of the environmental threats posed by the "greenhouse effect".[1] Although current amine scrubbing technology in industry has the advantages of good reactivity, high capacity, and low cost, an inherent drawback is that it produces and releases volatile organic compounds.[2] Thus, the discovery of new materials that can selectively and efficiently eliminate CO$_2$ is essential to realize practical carbon capture and sequestration. Ionic liquids (ILs) are the state-of-the-art solvent in this regard because of their unique properties, including extremely low volatility, high thermal stability, virtually unlimited tunability, and excellent affinity with acidic gases.[3,4]

In light of the chemistry of alkanolamines' reactivity with CO$_2$, grafting amine groups to the framework of ILs is a promising method of improving the absorption of CO$_2$ in ILs.[5–7] Davis et al.[5] reported the first example of amine-functionalized cation-tethered ILs for CO$_2$ capture, in which 0.5 mol CO$_2$ per mol of IL could be absorbed through a carbamate mechanism. Brennecke et al.[7a] further demonstrated that amino acid ILs, whose amine groups are tethered on anions in the vicinity of carboxylate groups, could capture almost 1 mol CO$_2$ per mol of IL by forming carbamic acid rather than carbamate. Subsequently, some other anion-functionalized ILs—including azolate ILs,[7e] phenolate ILs,[7f] methylbenzolate ILs,[7j] and pyridinolate ILs[7k]—have been examined as high-capacity absorbents for CO$_2$. Recently, capture of 2 mol CO$_2$ per mol of IL was achieved after 24–48 h by amino-functionalized amino acid ILs making use of two amino groups.[8] However, note particularly that carboxylate groups in amino acid ILs are almost deactivated to interact with CO$_2$. Generally, a carboxylate anion can complex with CO$_2$ very efficiently. The dilemma is that the negative inductive effect of an amino group tethered on anions reduces the alkalinity of a carboxylate group. For example, the pK_b of an acetate anion is 9.24, whereas the pK_{b2} of glycinate is 11.66. Thereby, the challenge remains regarding whether a new method of activating carboxylate groups in amino acid ILs to capture CO$_2$ effectively can be developed.

Herein, we propose a new method to activate carboxylate groups in amino acid ILs to attract CO$_2$ very efficiently. The essence of our strategy is to reduce the negative inductive effect of amino groups by introducing electron-withdrawing sites to amino acid anions. Thus, robust absorption of CO$_2$ (up to 1.69 mol CO$_2$ per mol IL) could be achieved for the first time through multiple-site interactions between amino and carboxylate groups in amino acid anions and CO$_2$. The chemical structures of five aminopolycarboxylate-based ILs (APC-ILs) designed in this work are shown in Scheme 1. The anions of the APC-ILs could be viewed as N-substituted glycinates. These structures were confirmed by nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and mass spectrometry. The physico-chemical properties were characterized by thermogravimetry-differential scan-



Scheme 1. Chemical structures of the anion and the cation in aminopolycarboxylate-based ionic liquids.

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[*] F. F. Chen,[+] Y. Zhou, Prof. Dr. D. J. Tao
College of Chemistry and Chemical Engineering, Jiangxi Inorganic Membrane Materials Engineering Research Centre, Jiangxi Normal University
Nanchang 330022 (China)
E-mail: djtao@jxnu.edu.cn
dtao1@utk.edu

Dr. K. Huang,[+] Dr. X. Zhu, Prof. Dr. D. J. Tao, Prof. Dr. S. Dai
Department of Chemistry, University of Tennessee
Knoxville, TN 37996 (USA)

Prof. Dr. S. Dai
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)
E-mail: dais@ornl.gov

Dr. Z. Q. Tian, Prof. Dr. D. Jiang
Department of Chemistry, University of California
Riverside, CA 92521 (USA)

[+] These authors contributed equally to this work.

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ning calorimetry (TG-DSC), viscometer, and densimeter. The characterization results are presented in the Supporting Information (Table S1).

We first determined CO_2 absorption in these five APC-ILs in relation to time (Figure 1). Surprisingly, it was seen that two APC-ILs showed very high capacity for CO_2 capture under atmospheric pressure, which is significantly greater than 1:1 stoichiometry. For example, for $[P_{4442}]_2[IDA]$, capture of 1.69 mol CO_2 per mol IL, corresponding to a gravimetric capacity of 13 %, was achieved at 40 °C and 1 bar. Moreover, the effect of the pressure and the temperature on CO_2 capture by $[P_{4442}]_2[IDA]$ was investigated (Supporting Information, Figure S1). It was seen that CO_2 capacity decreased from 1.69 to 1.33 mol per mol IL when the partial pressure decreased from 1 bar to 0.4 bar. The mole ratio of CO_2 to IL decreased to 1.09 upon increasing the temperature to 80 °C. Thus, the captured CO_2 was easy to release by heating or under reduced pressure. The repeated absorption of CO_2 in $[P_{4442}]_2[IDA]$ was carried out at 40 °C and 1 bar (Supporting Information, Figure S3). As can be seen, the absorption capacity of CO_2 remained unchanged after five cycles, indicating that this CO_2 capture process by $[P_{4442}]_2[IDA]$ is highly reversible. Also, there was no obvious change in the characteristic bands of IR and NMR spectra between the fresh and reused $[P_{4442}]_2[IDA]$ ILs (Supporting Information, Figures S4–S6), demonstrating that $[P_{4442}]_2[IDA]$ for CO_2 capture is stable enough to be recycled.

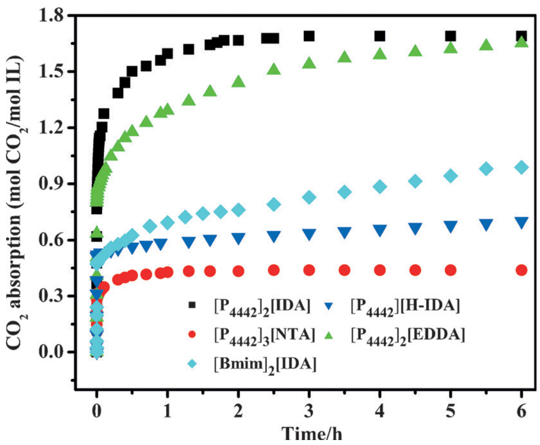


Figure 1. Absorption of CO_2 in the five synthesized APC-ILs over time at 40 °C and 1 bar.

Clearly, APC-IL $[P_{4442}]_2[IDA]$ has much higher absorption than traditional amino acid ILs (e.g., 0.52 for $[P_{4442}][Gly]$ and ca. 0.90 for $[P_{66614}][Pro]$) and is also superior to most functionalized ILs and adsorbent materials in terms of CO_2 capacity either in molar ratio or mass ratio (Table 1). As is well known, an amino group tethered on an anion has been proved to be able to complex with equimolar CO_2. Therefore, the solubility of CO_2 in [IDA]-based ILs exceeds the limit of 1 mol mol^{-1} apparently because carboxylate groups on the [IDA] anion function as additional active sites for attracting CO_2. Obviously, the difference between [IDA] and [Gly] is that only one more acetate group is substituted on the nitrogen of [IDA] relative to [Gly]. However, the solubility of CO_2 in $[P_{4442}]_2[IDA]$ is still much higher than the sum for $[P_{4442}][Gly]$ (0.52) and $[P_{4442}][Ac]$ (0.30), as presented in Table 1. Therefore, the highly enhanced CO_2 capacity of [IDA]-based ILs cannot be explained simply as a combination of the capacities of amino acid anions and acetate anions.

Table 1: Absorption capacity of CO_2 in APC-ILs and other functionalized ILs under 1 bar.

Ionic liquid	T [°C]	Solubility [mol/mol]	Solubility [g/g]	Ref.
$[P_{4442}]_2[IDA]$	40	1.69	0.13	–
$[Bmim]_2[IDA]$	40	0.99	0.11	–
$[P_{4442}][H\text{-}IDA]$	40	0.70	0.08	–
$[P_{4442}]_3[NTA]$	40	0.44	0.02	–
$[P_{4442}]_2[EDDA]$	40	1.65	0.11	–
$[P_{4442}][Gly]$	40	0.52	0.07	–
$[P_{4442}][Ac]$	40	0.30	0.05	–
$[P_{4442}][Gly]+[P_{4442}][Ac]$	40	0.82	–	–
$[P_{4442}]_2[Oxalate]$	40	0.53	0.04	–
$[P_{66614}][2\text{-}Op]$	20	1.58	0.12	[7k]
*i*PrNH-GlyNa[a]	25	0.91	–	[7h]
$[P_{66614}][PhO]$	30	0.85	0.06	[7f]
$[P_{66614}][Im]$	23	1.00	0.08	[7e]
[MTBDH][TFE]	23	1.13	0.19	[7b]
$[P_{66614}][Pro]$	22	ca. 0.9	0.07	[7a]
$[P_{66614}][2\text{-}CNpyr]$	40	ca. 0.7	0.05	[7g]
$[aP_{4443}][Gly]$[b]	45	ca. 1.1	–	[6c]
$[APbim][BF_4]$	25	ca. 0.5	0.08	[5]

[a] The absorption was carried out in PEG_{150} solution. [b] The absorption was carried out on SiO_2 supporter.

To illustrate the underlying mechanism, we employed density functional theory calculations at the B3LYP/6-311++G(d,p) level with a Gaussian 09 program[9] to investigate the interaction of [IDA], [Gly], and [Ac] anions with CO_2 (Figure 2). We found that after the amino group of [Gly] complexed with the first CO_2 ($\Delta H_1 = -68.7$ kJ mol^{-1}), a carbamic acid group was formed, sharing an intramolecular proton with the carboxylate group of [Gly]. That is to say, the shared proton weakened the basicity of the carboxylate group, and the electron-withdrawing amino group tethered in the vicinity of the carboxylate group further robbed its ability to attract CO_2. Thus, the strength of interaction between the carboxylate group of [Gly] and the second CO_2 ($\Delta H_2 = -19.6$ kJ mol^{-1}) was located in a range of weak physical absorption; for example, ΔH for $CO_2 + [Bmim][PF_6]$ is -16.1 kJ mol^{-1}.[4a] As a result, [Gly] cannot further attract a second CO_2 efficiently, and the limit of CO_2 solubility in amino acid ILs is always 1 mol mol^{-1}. However, comparing [IDA] with [Gly], the substituted acetate group of [IDA] can further interact with a second CO_2 very efficiently ($\Delta H_2 = -52.8$ kJ mol^{-1}) after the amino group complexes with the first CO_2 ($\Delta H_1 = -89.0$ kJ mol^{-1}). This value is much larger than the interaction of a free acetate anion with CO_2 ($\Delta H = -34.2$ kJ mol^{-1}, Supporting Information, Figure S7). More impressively, [IDA] can even attract a third and fourth CO_2 moderately around the carboxylate groups ($\Delta H_3 = -25.4$ kJ mol^{-1} and $\Delta H_4 = -22.1$ kJ mol^{-1}). These interactions are also larger than the secondary interaction of [Gly] with

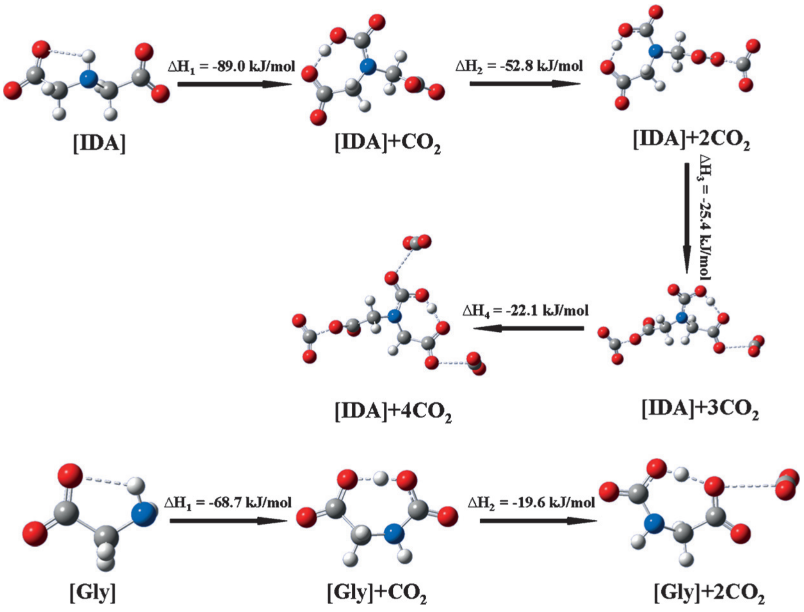


Figure 2. Multiple-site interaction of [IDA] and [Gly] anions with CO_2. O red, N blue, C gray, H white.

CO_2 ($-19.6\ kJ\,mol^{-1}$). Accordingly, the multiple-site interactions between CO_2 and [IDA] were confirmed by the experimental enthalpy of CO_2 absorption at different absorption capacities, which is determined from the isotherms of CO_2 absorption (Supporting Information, Figure S2). Thus we believe there must be a positive cooperative effect between the substituted acetate group and the amino group of [IDA], resulting in the significant increase in CO_2 capacity.

Thereafter, we calculated the natural bond orbital (NBO) atomic charges of nitrogen, oxygen, and hydrogen in the anion, and the complex of the anion with CO_2. As shown in Figure 3, the proton shared by the carboxylate and carbamic acid in the complex possessed much more positive charge than that in the amine group, leading to the deactivated carboxylate group. We can estimate the CO_2 affinity of each carboxylate group from the absolute value of the sum of NBO charges of the two oxygen atoms, which is termed as $|\Sigma eO|$.[10] Larger $|\Sigma eO|$ relates to a more negative charge distribution of the carboxylate group and stronger interaction with CO_2. In [Gly], $|\Sigma eO|$ is $1.596|e|$. After complexing with CO_2, it decreased by $0.103|e|$, which was close to the increased positive charge of the proton ($0.123|e|$). The reduced negative charges of oxygen atoms weakened the affinity of the carboxylate with CO_2. Similarly, the shared proton in the $[IDA]+CO_2$ complex also resulted in the $|\Sigma eO|$ of one carboxylate group decreasing from $1.629|e|$ to $1.556|e|$. But the other carboxylate group was influenced insignificantly; therefore it could still complex with one more CO_2. Moreover, the NBO atomic negative charges of the nitrogen atoms in [IDA] and of the complex of $[IDA]+CO_2$ decreased significantly compared with those in [Gly] and the complex of $[Gly]+CO_2$, respectively. More negative charges coming from the nitrogen atoms concentrated on the oxygen atoms in [IDA] and the complex of $[IDA]+CO_2$. This shows that introducing an electron-withdrawing substituted acetate group can effectively reduce the negative inductive effect of an amino group in [IDA], thereby leading to an enhanced interaction between the carboxylate group in [IDA] and CO_2. Hence, unlike the deactivated carboxylate group in [Gly], the carboxylate groups in [IDA] are activated to attract CO_2 very efficiently, which enables [IDA] to have multiple-site interactions with CO_2.

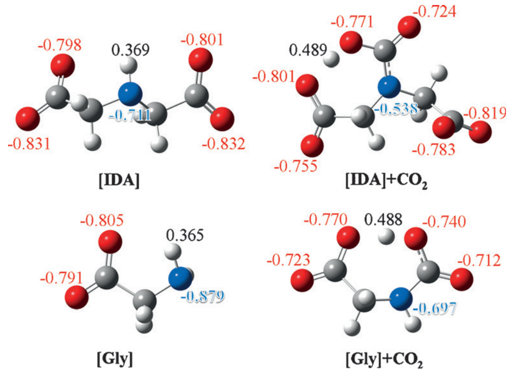


Figure 3. The NBO atomic charges of nitrogen, oxygen, and hydrogen in the anion, and the complex of the anion with CO_2 (blue N, red O, white H).

The multiple-site interaction between [IDA] and CO_2 was further verified by Fourier transform infrared (FTIR) and ^{13}C NMR spectroscopy (Figure 4). In the IR spectrum, the N−H stretch of [IDA] observed at $3347\ cm^{-1}$ disappeared after CO_2 absorption. Simultaneously, two new characteristic peaks were observed at $1630\ cm^{-1}$ and $1423\ cm^{-1}$, which can be assigned to the asymmetrical stretching vibration of carbamic acid in the $NH{-}CO_2$ interaction and the carbonate ion in the $O{-}CO_2$ interaction, respectively. In contrast, only one new peak appeared at $1689\ cm^{-1}$, which corresponds to carbamic acid after CO_2 absorption by $[P_{66614}][Pro]$.[7a] Furthermore, it is seen in Figure 4b that one new signal in the ^{13}C NMR spectra at $\delta = 160.2$ ppm appeared when [IDA] captured 0.8 mol CO_2 per mol IL, which is clearly indicative of carbamic acid formation between NH and CO_2. Subsequently, after 1.69 mol CO_2 uptake per mol IL, two new resonances were observed at $\delta = 156.8$ and 163.5 ppm, respectively. The first new peak at $\delta = 163.5$ ppm could likewise be assigned to carbamate carbonyl carbon atom. The second new resonance at $\delta = 156.8$ ppm was attributed to the secondarily captured CO_2, which was thought to form a carbonate anion as a result of the strong interaction of CO_2 with the carboxylate group in [IDA]. Accordingly, the resonance of carboxylate carbons in [IDA] at $\delta = 171.8$ ppm split into two peaks at $\delta = 169.2$ and 174.4 ppm because of the different chemical environments after one of the carboxylate groups in [IDA] captured a second CO_2. Therefore, on the basis of previous reports[7] and the observed product, a plausible mechanism of CO_2 absorption by [IDA] can be proposed (Scheme 2), which exhibits a two-site interaction between [IDA] and CO_2.

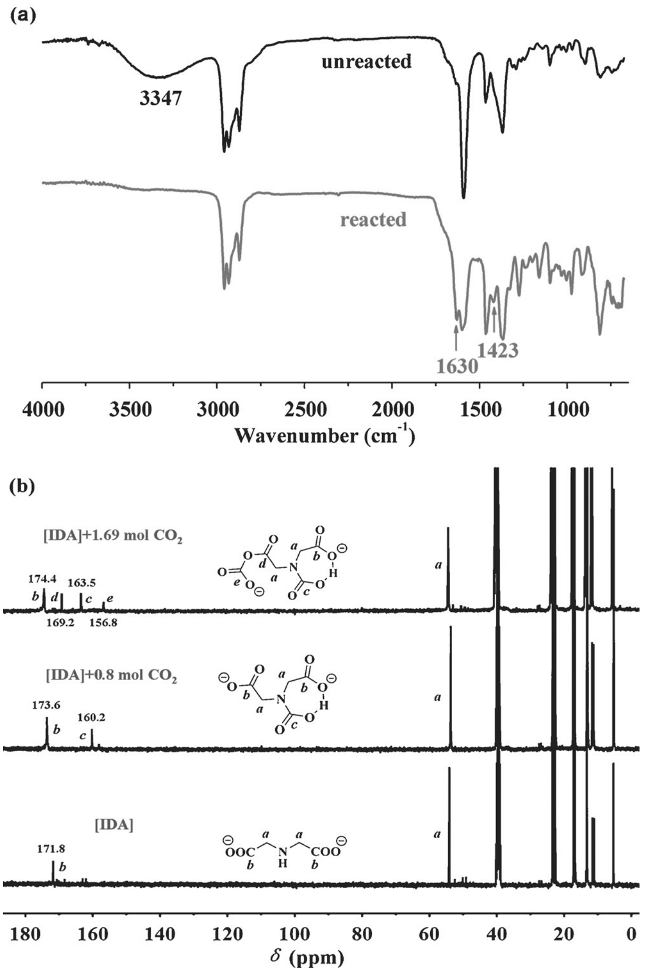
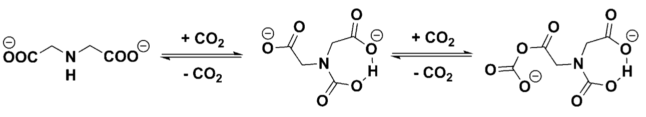


Figure 4. a) FTIR and b) ^{13}C NMR spectra of APC-IL $[P_{4442}]_2$[IDA] before and after the capture of CO_2.

On the basis of these results, another APC-IL $[P_{4442}]_2$[EDDA] also had a very high CO_2 capture capacity (1.65 mol CO_2 per mol IL). Its multiple-site interactions with CO_2 are shown in Figure S8 in the Supporting Information. However, for $[P_{4442}]$[H-IDA]—in which an acetic acid group, not an acetate group, was substituted on the nitrogen of the amino group—absorption capacity for CO_2 was only 0.70, similar to that of $[P_{66614}]$[Pro]. The binding energies of [H-IDA] with the first and second CO_2 were -39.4 and -13.7 kJ mol^{-1}, respectively (Supporting Information, Figure S9). The NBO charges calculations indicated that after the uptake of the first CO_2, $|\Sigma eO|$ of the acetic acid group in the complex of [H-IDA] + CO_2 decreased significantly from $1.506|e|$ to $1.306|e|$ because of the formation of intramolecular hydrogen bonds (Supporting Information, Figure S10), so that the acetic acid group in [H-IDA] cannot capture a second CO_2 efficiently. $[P_{4442}]_3$[NTA] also showed a relatively low CO_2 absorption capacity (0.44 mol CO_2 per mol IL) because of the lack of proton in the tertiary amine group. In addition, $[Bmim]_2$[IDA], which has the same anion of [IDA] as that of $[P_{4442}]_2$[IDA], exhibited the absorption capacity of only 0.99 mol CO_2 per mol IL. This is attributed to the difference caused by CO_2 absorption in viscosities. It was seen that the viscosity of $[Bmim]_2$[IDA] increased significantly from 627.7 cp to 17346 cp after the capture of CO_2, whereas the viscosity of $[P_{4442}]_2$[IDA] increased only to 961.6 cp upon complexation (Supporting Information, Tables S2,S3). For $[P_{4442}]_2$[IDA], it is difficult to form the intermolecular hydrogen-bonded network because of the absence of any acidic proton in the cation $[P_{4442}]$. In contrast, the C2-H of [Bmim] could form strong intermolecular hydrogen bonding with carbamic acid after the capture of CO_2 and result in the dramatic increase in viscosity, thus leading to a lower CO_2 capacity.[7e,11]



Scheme 2. The proposed mechanism of CO_2 absorption by $[P_{4442}]_2$[IDA] through multiple-site interactions.

In summary, we have introduced a new strategy for multimolar absorption of CO_2 by activating a carboxylate group in APC-ILs. Thus, extremely high CO_2 capacities (up to 1.69 mol CO_2 per mol IL) were achieved through multiple-site interactions between the amino group and carboxylate group in APC-ILs. Quantum-chemical calculations and spectroscopic investigations show that the reduction of the negative inductive effect of amino groups in APC-ILs can stimulate the carboxylate group to attract CO_2 very efficiently, resulting in a significant increase in CO_2 capacity. We believe that this highly efficient and reversible process by APC-ILs has great potential for the capture of CO_2.

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